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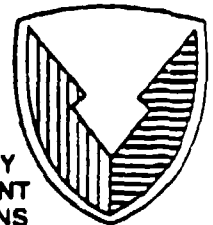
CRDEC-TR-87048

THE APPLICATION OF SOLID STATE
PHYSICS PRINCIPLES TO PYROTECHNIC
MIXTURE SYSTEMS

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MUNITIONS DIRECTORATE

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PREFACE

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THE APPLICATION OF SOLID STATE PHYSICS PRINCIPLES TO PYROTECHNIC MIXTURE SYSTEMS

1. INTRODUCTION

Pyrotechnics, a fine art (from the Greek words pyr (fire) and techne (an art)), is one of three closely related technologies: explosives, propellants, and pyrotechnics proper.

Explosives perform at the highest speed of reaction, leaving gaseous products; propellants are gas formers and have brisk reactivity, but are slower than explosives; pyrotechnic mixtures react mostly at visibly observable rates resulting in the formation of solid residues.

Chemical reactions require heat input throughout the whole process (endothermic reactions), or they give off heat (exothermic reactions). The heat released in the latter case may be insufficient to cause a self-sustaining reaction, or it may produce flame or glow throughout the substance or substances either at high reaction speeds, or slowly, making it suitable for pyrotechnical purposes. Pyrotechnics are nearly exclusively concerned with solid ingredients, while explosives and propellants may be solids or liquids. An exothermic reaction may be either the result of an interaction of two or more substances or stem from the decomposition of a single compound. Interaction between solids is the rule in pyrotechnics and decomposition in explosives, while typical propellants are of either one.

A pyrotechnic process differs from ordinary combustion because it does not require ambient air. Once the pyrotechnic is triggered by a small external force, it may take its course in complete isolation from external chemical influences.

The mechanism of combustion of a pyrotechnic composition was studied by Shidlouskiy¹ and described the scheme shown in Figure 1.²

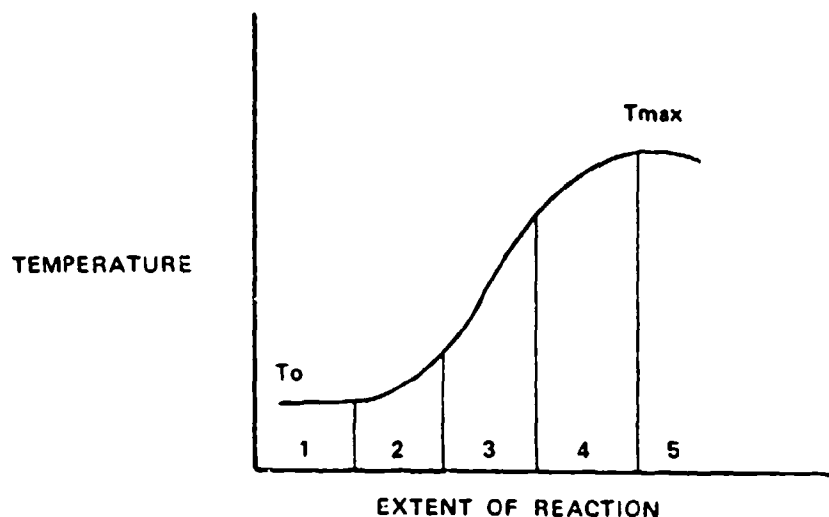
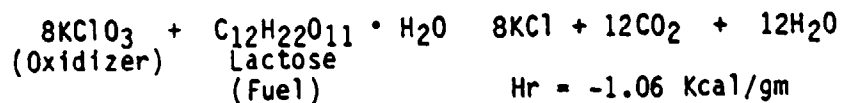
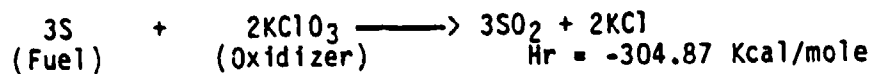


Figure 1. Diagram of Combustion of Pyrotechnic Composition

The regions 1 to 5 are the zones of initial composition, heating, reaction in the condensed phase, reaction in the gas phase, and reaction product, respectively.

Two examples of simple pyrotechnic reactions are as follows:



The heat from these reactions is used to aerosolize/vaporize dyes, riot control agents, thermite, and flame mixtures.

Figure 2 shows two typical pyrotechnic devices/designs: an end burner and a center burner for typical pyrotechnic mixtures.

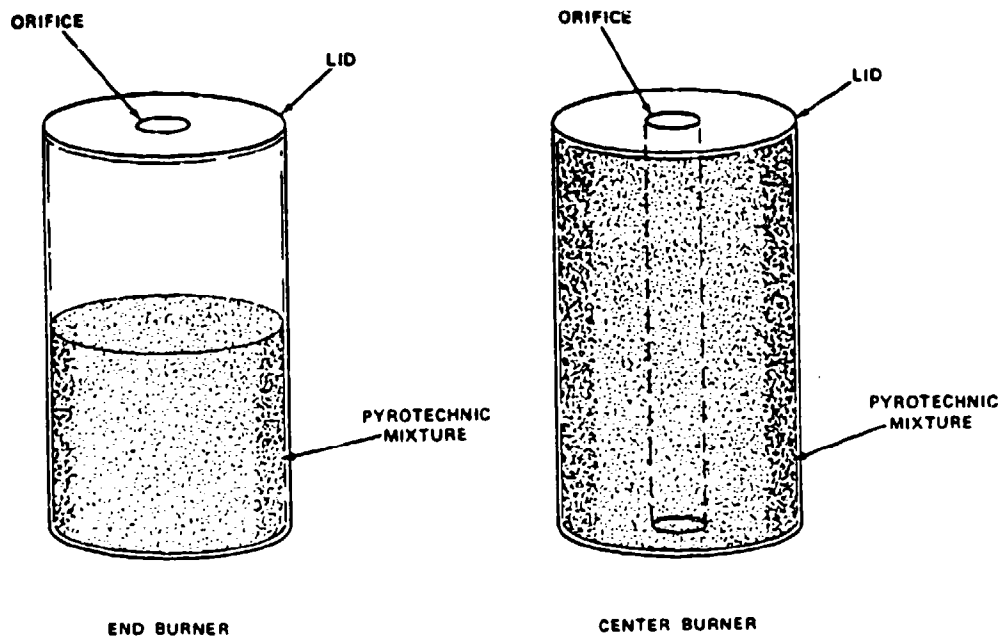


Figure 2. Typical Pyrotechnic Devices

There are many variables/parameters that affect the functional performance of a pyrotechnic mixture. Some of these are: thermal conductivity, particle size, loading density/pressure, degree of confinement, and ratio of oxidizer to fuel.

2. THE SOLID STATE

The solid state is characterized by a definite shape and volume. The observed shape will be the one that maximizes favorable interaction between the atoms, ions, or molecules making up the structure.

Solids lacking an ordered, crystalline arrangement are termed amorphous materials and resemble rigid liquids in structure and properties.

In the crystalline solid state, there is little vibrational or translational freedom and, hence, diffusion into a crystalline lattice is slow and difficult. As the temperature of a solid is raised by the input of heat, vibrational and translational movement occurs. A particular temperature, the melting point, is obtained. This motion overcomes attractive forces holding the lattice together and the liquid state is produced. Table 1 categorizes the types of solids according to the particles that make up the crystalline lattice.

Table 1. Types of Crystalline Solids³

Type of solid	Units comprising crystal lattice	Attractive force	Examples
Ionic	Positive and negative ions	Electrostatic attraction	KNO ₃ , NaCl
Molecular	Neutral molecules	Dipole-dipole attractions, plus weaker, nonpolar forces	CO ₂ (dry ice), sugar
Covalent	Atoms	Covalent bonds	Diamond (carbon)
Metallic	Metal atoms	Dispersed electrons attached to numerous metal atom nuclei	Fe, Al, Mg

2.1 Influence of the Solid State Ignition and Propagation of Pyrotechnic Composition.

In order for a pyrotechnic mixture to ignite and propagate, heat must be conducted along a column of the mixture. Hot gases serve as excellent heat carriers, but frequently the heat must be conducted by the solid state, ahead of the reaction zone. Heat can be transferred by molecular motion as well as by free mobile electrons.

2.2 Thermal Conductivity.

For a column of pyrotechnic composition to burn smoothly, the reaction zone must readily travel down the length of composition. Heat is transferred from layer to layer, raising the adjacent material to the ignition temperature of the particular composition. Good thermal conductivity can be essential for smooth propagation of burning, and this is an important role played by metals/metal salts in many mixtures. Metals are the best conductors, with organic compounds ranking among the worst.

Observing Table 2,⁴ one can see how the presence of a small quantity of metal powders in a pyrotechnic composition can greatly increase the thermal conductivity of the mixture and thereby increase the burning rate (length/time) or decrease the burning time.

Table 2. Thermal Conductivity Values for Solids⁴

Material	Thermal conductivity (x 10 ³), cal/sec-cm-°C
Copper	910
Aluminum	500
Iron	150
Glass	2.3
Oak wood	0.4
Paper	0.3
Charcoal	0.2

2.3 Catalysts.

Table 3 shows the effect of metallic powders on the burning time of pyrotechnic mixtures containing potassium chlorate, ethylene bis(isothiosemicarbazide) (EBS), and a glycolate organic salt. The four metal powder catalysts lowered the emission time from 20% to 30% without significant change in the yield of generated glycolate.

Table 3. Catalysis Effect⁵

Catalyst	Emission time sec
Reference X	10.1
	10.3
	10.4
	10.3
	10.4
Average	10.3
standard deviation	0.12
Ferric acetyl acetonate	7.1
	7.3
	7.4
	7.2
	7.1
Average	7.2
Standard deviation	0.13
Ferric sulfide	8.0
	8.2
	8.4
	8.3
	8.2
Average	8.2
Standard deviation	0.15
Ferric Oxide	7.1
	7.3
	7.4
	7.2
	7.1
Average	7.2
Standard deviation	0.13
Cupric chloride	7.0
	7.3
	7.2
	7.1
	7.4
Average	7.2
Standard deviation	0.16

The rate of flow of heat through the specimen is equal to the rate of heat transfer, expressed by:

$$\frac{KA(T_1-T)}{X} = Mc \frac{dT}{dt}$$

K = Thermal conductivity of the material

A = Area of upper block of conductivity material or heat sink

T₁ = Constant temperature of the heat source

T = Temperature of face of material in contact with heat sink

X = Thickness of specimen

M = Mass of the heat sink

C = Specific heat of the heat sink

$\frac{dT}{dt}$ = Rate of increase of temperature of the heat sink.

See Figure 3 for illustration of apparatus for measuring thermal conductivity.

A final example of the effects of thermal conductivity, the burning rate (emission time of pyrotechnic mixtures) is shown in Table 4.

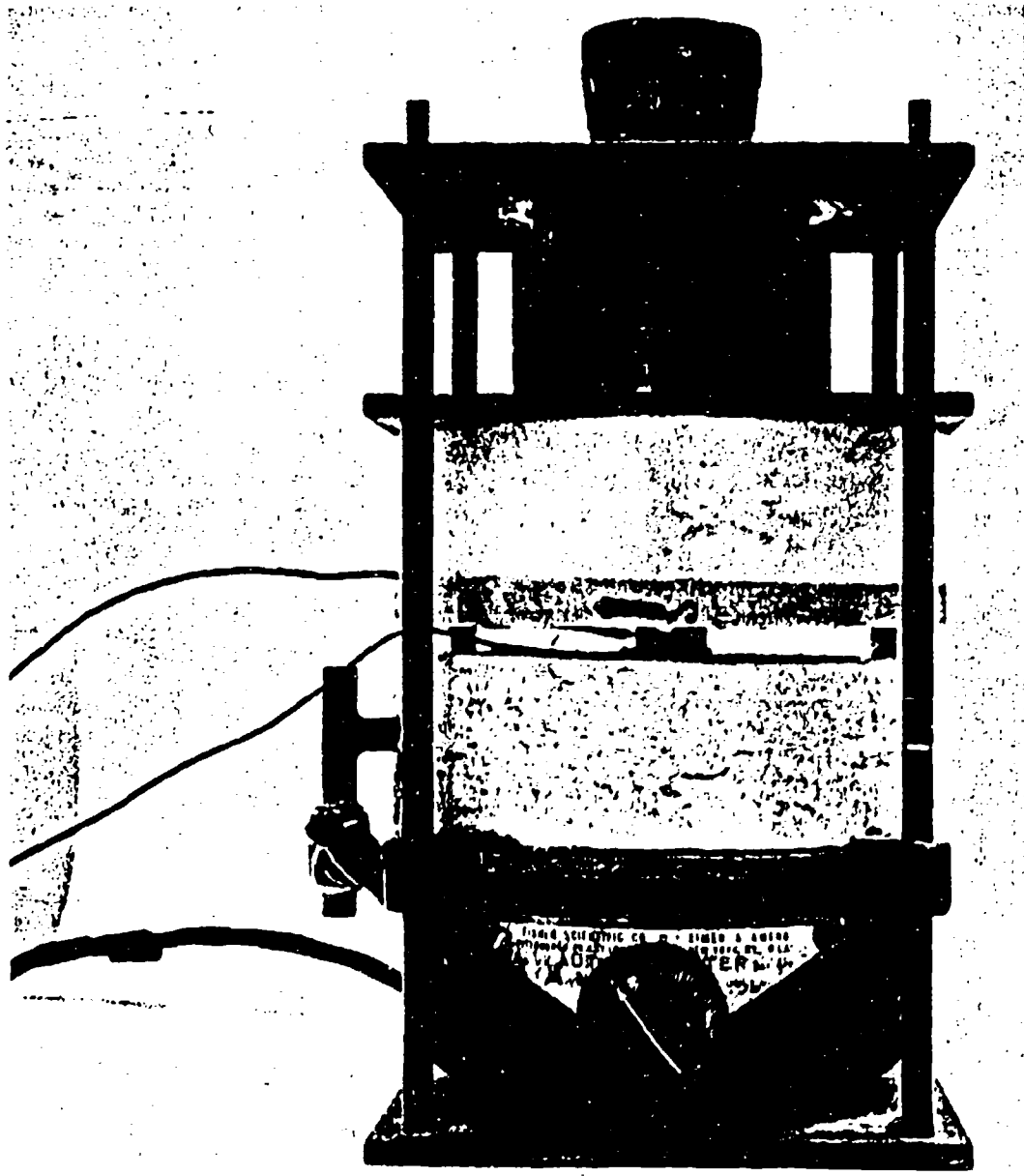


Figure 3. Apparatus for Measuring Thermal Conductivity

Table 4. Effect of Burning Rate Catalysts⁴

Catalysts	Burning Rate (in./sec)
Control (no catalyst)	0.017
Copper chromite	0.013
Cu ₂ O	0.011
FeS	0.012
Fe ₃ O ₄	0.012
MnO ₂	0.011
Ferric octoate	0.011
Ferrocene	0.017
Fe ₂ O ₃	0.012
CuO	0.012
Ferric acetyl acetoate	0.012
Chrome green	0.013
K ₂ Cr ₂ O ₇	0.015
N-butyryl ferrocene	0.012

The standard mixture of 40.6% orthochlorobenzal malononitrile, 3.2% nitrocellulose, 11.6% kaolin, 19.4% lactose, and 25.2% KClO₃ was studied with 1% metal powder added. These results show that no burning rate enhancement is obtained; instead, depression of the burning rate was common. These results disagree with those observed previously for the glycolate mixtures. The probable cause is possible reaction between the metal powder and orthochlorobenzal malononitrile.

3. PARTICLE SIZE

Homogeneity and pyrotechnic performance will increase as the particle size of the various components is decreased. The finer the particle size, the more reactive a particular composition should be, with all other factors held constant. For a high-energy reaction to rapidly proceed, the oxidizer must be in intimate contact with the fuel. Decreasing the particle size will increase the intimate contact between particles. Increasing the particle size, especially in a nonmetallic mixture, which is pressed at a constant loading pressure, increases the burning rate. The phenomenon occurs because of the number of

void spaces formed. The void spaces/areas increase with increasing particle sizes. Hence, the hot gases (flame front) traveling through the pyrotechnic mixtures will find more voids with large particle size packing; thus reducing the burning/emission time and consequently increasing the burning rate for nonmetallic mixtures.

A smooth sphere will possess the minimum surface area for a given mass of material. An uneven, porous particle will exhibit much more free surface and, consequently, will be a much more reactive material.

Ease of initiation depends on the particle size. This factor is important for metallic fuels with melting points higher than or comparable to that of the oxidizer. Some metals, including aluminum, magnesium, and titanium, can be quite hazardous when present in fine particle sizes during processing. Larger particle sizes are used with metallic mixtures to minimize accidental ignition and decrease the burning time.

Figure 4 is a plot of particle size versus emission time for a smoke-producing pyrotechnic mixture containing $KClO_3$, ethylene bis (isothiosemicarbide) (EBS) (organic fuel) and a glycolate salt mixture. This mixture contains no metal particles of spherical shape where sphericity is close to 1. The materials are organic/inorganic salts with irregular particle sizes. A decrease in the burning/emission time as a function of the particle size is noted. The mixtures were pressed at $1,130 \text{ kg/cm}^2$ constant load force and an equation for the curve, $Y = 19.587 X^{-0.173}$, was obtained. This relationship does not follow the trend for most metallic powdered mixtures, which are described below. For metals, the important phenomenon is thermal conductivity, which allows rapid transport of heat through the mixture.

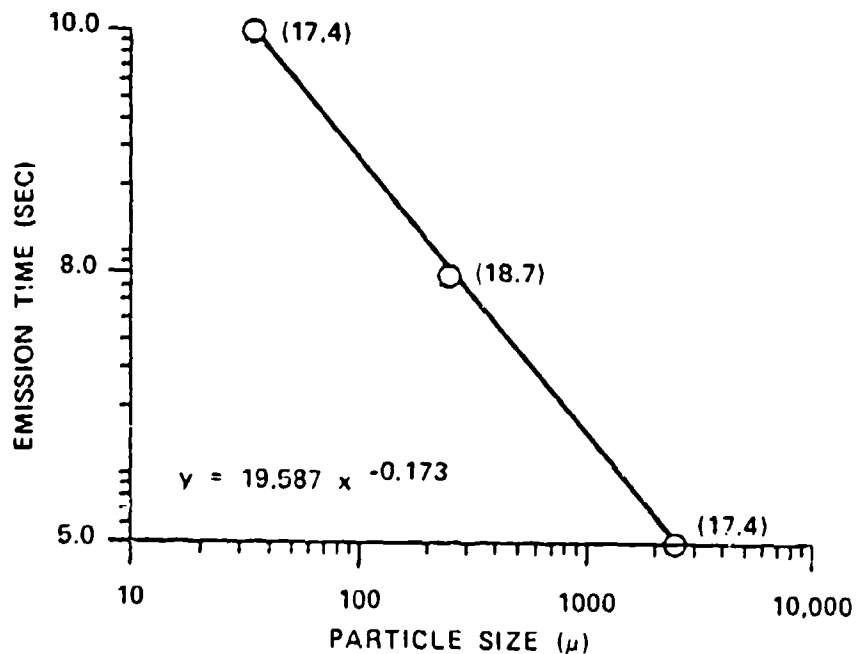


Figure 4. Emission Time Versus Particle Size

Tables 5 and 6 show the effect of metal particles (magnesium and titanium) on flare mixtures. An opposite effect of particle size is observed here, as opposed to when irregularly shaped particle granules of the previously discussed organic/inorganic salt mixture are burned. The burning rate/emission time is affected by the magnesium and titanium particle sizes. These metals are very nearly spherical in shape and are good heat conductors. The smaller these particles are, the more available the surface areas for heat transfer through the mixture.

Table 5. Effect of Particle Size on Performance of a Flare Composition⁶

Composition: Component	% by weight	Average particle size
Magnesium metal	48	See table below
Sodium nitrate, NaNO ₃	42	34 micrometers (10 ⁻⁶ meters)
Laminac binder	8	-
Polyvinyl chloride	2	27 micrometers

Magnesium average particle size, micrometers	Flare candlepower (1,000 candles)	Flare burning rate inches/minutes
437	130	2.62
322	154	3.01
168	293	5.66
110	285	5.84

Table 6. Effect of Particle Size on Burning Rate⁶

		By weight %
Composition:	Titanium metal	48
	Strontium nitrate	45
	Linseed oil	4
	Chlorinated rubber	3

Titanium size range micrometers	Relative burning rate inches/minutes
Less than 6	1.00 (fastest)
6-10	0.68
10-14	0.63
14-18	0.50
Greater than 18	0.37 (slowest)

The final effect of particle size will be seen on the heat of reaction for a 50:50 red lead to ferrosilicon mixture (reported by Nakahara and cited by McLain⁶), as shown in Table 7.

Table 7. Effect of Particle Size on Reaction

Fe-Si mean particle size, μ	22	16	14	9.3	8.0	6.2
Heat of reaction, cal/gm	176.7	182.5	185.2	189.3	192.2	196.8

Naeser and Scholz (cited by McLain⁶) provided a plausible explanation for the reaction $\text{Fe}_2\text{O}_3 + \text{SiO}_2 \longrightarrow \text{Fe}_2\text{SiO}_5$. These investigators also passed powders through a rolling mill just before testing. Some of their findings were that:

- Rolled dolomite sintered at a temperature 100 to 150 °C lower than unrolled dolomite of the same particle size;

- The reaction temperature of the above reaction is as much as 200 °C lower for rolled than for unrolled reactants.

These results tend to support the hypothesis that milling enhances reactivity; not so much by particle size reduction as by lattice deformation, although the two may be unavoidably linked.

4. LOADING PRESSURE

There are generally two rules that describe the effect of loading pressure on the burning rate/emission time of a pyrotechnic mixture. If the pyrotechnic reaction is in the continued propagation stage (propagated via hot gases), then too high a loading pressure will retard the passage of hot gases along the column of the composition (Figure 5). This figure shows the plot of emission time in seconds versus the load force for the pyrotechnic mixture composed of $KClO_3$, EBS (organic fuel), and glycolate (organic salt). As the load force increases, hot gases are less rapidly transferred through the mixture, thus increasing the emission time. If the propagation of the pyrotechnic mixture is a solid-solid or solid-liquid phenomenon with the involvement of gas-phase components, then an increase in the loading pressure should lead to an increase in the burning rate. An example of this possibility is given in Table 8.

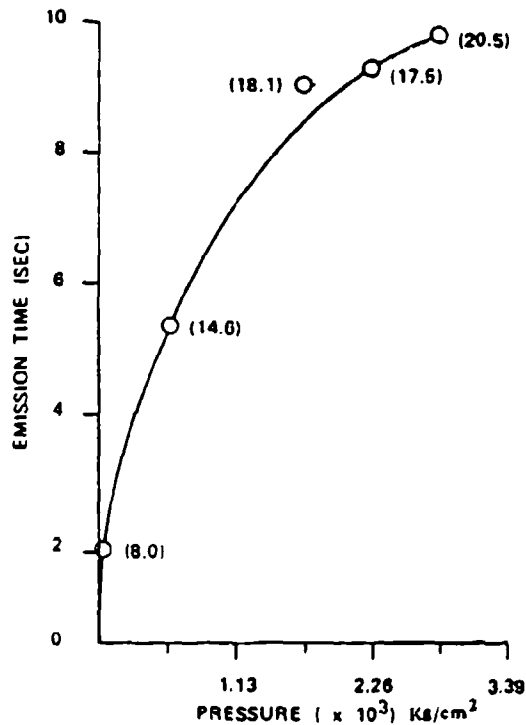


Figure 5. Emission Time Versus Loading Pressure

Table 8. Effect of Loading Pressure on the Burning Rate of a Delayed Mixture

Composition: Barium chromate, BaCrO ₄ , 90	
Boron 10	
Loading pressure (1000 psi)	Burning rate (seconds/gram)
36	.272 (fastest)
18	.276
9	.280
3.6	.287
1.3	.297
0.5	.309 (slowest)

The most pertinent effect overlooked in our two examples is the effect of loading pressure on the packing density of the mixture. Inherent in the packing density are void spaces between particles. Therefore, an increase in loading pressure decreases the void spaces, thus increasing the packing density. In the two examples of organic salts and metal/metal salt mixtures, an increase in the load force for the organic salt mixture resulted in an increase in the packing density (Figure 5), thus reducing the void area and reducing heat transfer through the mixture. In the case of the BaCrO₄/boron mixture (Table 8), an increase in the loading pressure also resulted in an increase in the packing density. However, since metals/metal salts are excellent thermoconductors, the tighter the packing, the better the heat transfer.

5. EFFECT OF CONFINEMENT

The effect of confinement on the burning rate of a solid mixture of constant particle size is shown in Figure 6. This curve shows that smaller port size gives faster burning. This is a gassy composition of KClO₃, ethylene bis (isothiosemicarbazide) (EBS), and a glycolate salt. As the exhaust port diameter on an end burner or cylindrical burning device is decreased, there is an increase in pressure in the void volume above the burning mixture, thus increasing the molecular collision of gas molecules and solid aerosol particles.

6. THERMAL PROPERTIES

As a solid pyrotechnic mixture absorbs heat energy from the moving flame front, the temperature rises and its internal energy, E, increases. The internal energy in most solids is composed primarily of the vibrational energy of the molecules and atoms and the kinetic energy of free electrons. One principal way of observing lattice vibrations is to measure the heat capacity directly or indirectly as the thermodynamic principle of heat capacity at constant pressure:

$$C_p = \frac{(H)P}{T}$$

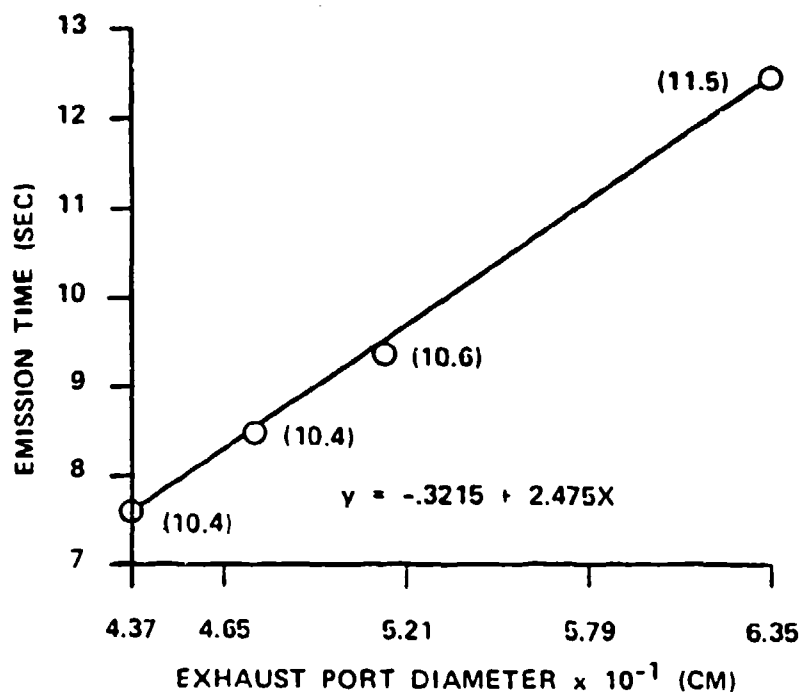


Figure 6. Emission Time Versus Exhaust Port Diameter

For pyrotechnic mixture studies, the ratio of oxidizer to fuel generally describes the heat of reaction, and this phenomenon is shown in Figure 7 for the $KClO_3$, EBS, and glycolate salt mixture. The point at 2.5/1 oxidizer/fuel is the optimum (stoichiometric ratio of the oxidizer to fuel). As we move away from this ratio, the emission time decreases for this solid mixture. Hence, the heat capacities are different for each mixture ratio.

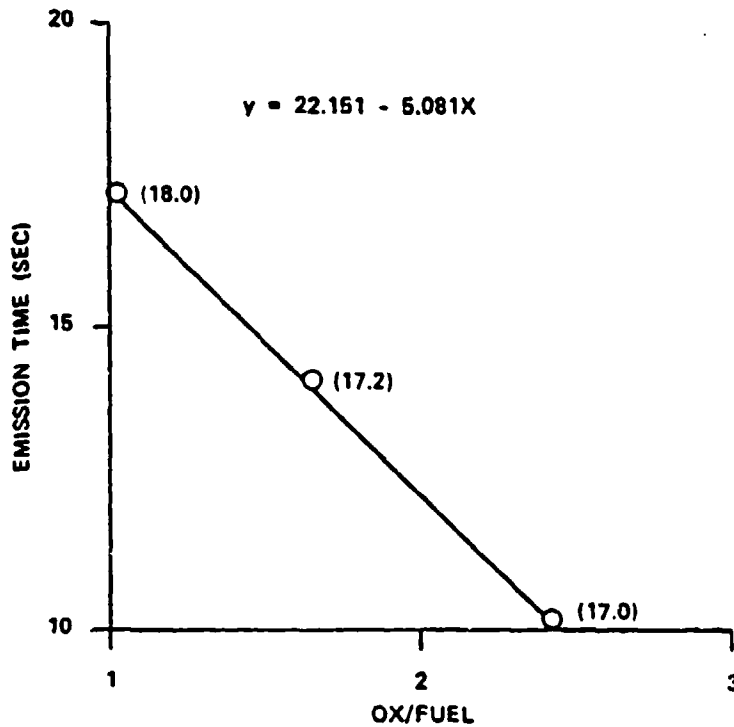


Figure 7. Emission Time Versus Oxidizer/Fuel

7. CONCLUSION

The burning rate/emission time of pyrotechnic mixtures is affected by the thermoconductivity, particle size, load density, degree of confinement, and the heat capacities of the mixtures. In the design/manufacture of the mixture systems, these parameters have to be optimized in order to obtain the desired characteristics of the mixture.

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